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GaN ceramics obtained by fusing of nanocrystalline GaN powder at high pressures and temperatures as substrate for growth of GaN epilayers

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Abstract

In this paper, we have grown GaN films by metalorganic chemical vapor-phase epitaxy (MOVPE) on GaN ceramics obtained from nanocrystalline powder of different initial grain sizes. The samples have been investigated by X-ray diffraction (XRD) and photoluminescence (PL). XRD reveals that the MOVPE GaN films are of single-phase wurtzite structure. Also, it has been observed that the PL spectrum is different for the GaN films compared to that for the GaN powder and also depends on the initial grain sizes.

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1. Introduction

GaN and related III–V nitride materials have been investigated for various applications in electronic and optoelectronic devices, such as blue and green light-emitting diodes, laser-diodes, and high-power and high-temperature electronic devices [1,2]. Although the growth of group III-nitride materials has progressed rapidly, it is still difficult to obtain simultaneously cost-effective and high-quality films. In order to obtain high-quality GaN films an epitaxy, a growth on a substrate with the same or very close lattice constant as GaN, seems to be necessary. However, the lack of such a substrate limits this approach to homoepitaxy, which needs bulk-like GaN substrate. Usually, GaN layers are grown on sapphire, SiC or other alternative substrates whose lattice constant is far from the lattice constant of GaN. In the case of such a hetero-epitaxy, the optical quality of these layers is usually worse due to the lattice mismatch, which generates structural defects introducing numerous energy levels in the gap [3].

However, for some applications, e.g. luminophors, such a quality of GaN layers is sufficient, but still the cost of the substrate seems to be too high in comparison to the obtained poor quality of the GaN layers.

Thus, in this work, we present the structural and optical properties of metalorganic chemical vapor-phase epitaxy (MOVPE) grown GaN films deposited onto alternative GaN ceramic substrates obtained from the GaN nano-crystalline powder.

2. Experimental procedure

In the first step, GaN nanosized powders were synthesized by the combustion method with some modifications. The preparation procedure was divided into two main steps—the first one is the hydrothermal processing using a microwave reactor, and the second is the synthesizing of

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the GaN nanocrystalline powder by using a horizontal quartz reactor with the NH_3 flow and heating the material to the required temperatures of 850 and 1050 °C. More details about the powder preparation can be found in our previous works [4,5].

During the conduction of the second step, the powder samples are fused into continuous ceramic layers. The fabrication of the GaN nanoceramics by means of the low-temperature–high-pressure (LTHP) technique was performed under 6 GPa at 800 °C for 1 min. In this manner two samples, characterized by the different sizes of the grains, were fabricated. The samples of GaN nanoceramics were black in color, with an average density of $\sim 5.5\,g/cm^3$ and with surface area measured with the multipoint Brunauer–Emmett–Teller technique $\|BET|\sim 10.5\,m^2/g$. More details about substrate properties as well as about similar substrates obtained at low temperature and at low pressure could be found elsewhere [6,7].

In the third step, GaN layers were grown on GaN ceramics in a horizontal flow MOVPE system. The low-frequency (40 kHz) inductive heating method was used to raise the temperature of the graphite susceptor up to 1020 °C. Trimethylgallium (TMGa) and ammonia (NH_3) were used with H_2 carrier gas. Before the growth process, the substrate was decreased in organic solvents and etched in a solution of $HF:H_2O$ (1:10). The substrate was annealed in the growth chamber for 10 min at 600 °C in H_2/NH_3 (1:1) ambient. The NH_3 was introduced at 450 °C during heating to prevent the decomposition of the GaN nanocrystalline powder substrate [8,9]. Then, the low-temperature GaN layers were grown during the temperature ramping from 600 to 850 °C for 5 min with 9300 V/III molar ratio. Next, the temperature was gradually increased to 1020 °C for 10 min. During the second temperature ramp, the low-temperature GaN buffer layers were annealed in NH_3/H_2 ambient (1:1). The high-temperature GaN layers were grown with 2200 V/III molar ratio at 1020 °C for 60 min. These experimental conditions were selected as the optimal for GaN layers' growth on monocrystalline GaN substrates at our epitaxial system. As a result, the nominally 3-μm-thick MOVPE layers were obtained on nanocrystalline GaN powder substrates.

Overall phase compositions of the nanopowders were determined by X-ray powder diffraction (XRD) with a Siemens D5000 diffractometer and $CuK_{\alpha 1}$ radiation, $\lambda = 0.15406$ nm. The structural investigations of the GaN thick-film and substrate have been carried out using a Philips MRD–HRD diffractometer and the same $CuK_{\alpha 1}$ radiation source.

For photoluminescence (PL), a 300 nm line of an argon laser has been used as a pump beam with $\sim 10\,kW/cm^2$ excitation power. An Ocean Optics HR4000 spectrometer was applied to collect the emission signal.

3. Results and discussion

Fig. 1 shows the XRD patterns of GaN powders obtained at two nitridation temperatures, 850 and 1050 °C. In both cases, XRD patterns show the diffraction lines which can be attributed to the formation of a hexagonal GaN with the wurtzite-type structure (JCPDS file no. 02–1078). By means of the Scherrer formula we

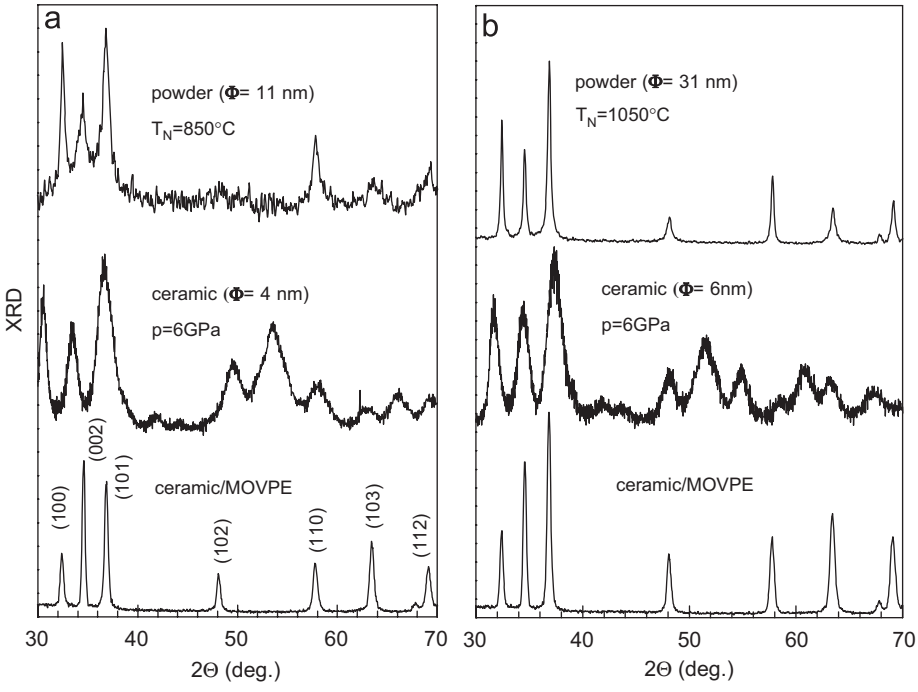

Fig. 1. X-ray diffraction patterns of (a) GaN powder obtained at 850 °C, GaN ceramic, a GaN film grown by MOVPE on GaN ceramic and (b) GaN powder obtained at 1050 °C, GaN ceramic, GaN film grown by MOVPE on GaN ceramic.

have determined that the average size of GaN grains is 11 and 30 nm for grains obtained at 850 and 1050 °C, respectively. In the case of the GaN powder after the compression process, the XRD spectrum changes significantly. Grain sizes, which are obtained using the Scherrer formula, are comparable for both samples and equal $\sim 5 \pm 1$ nm. The observed size reduction of the GaN grain after the compression process can be related to the strong deformation of GaN grains and amorphization of the surface layer of the grains or other phenomena.

Finally, we treat the compressed wafer as a substrate for the MOVPE-deposited GaN layer. XRD spectra of MOVPE GaN films are completely different from the XRD spectra of the powder samples and the spectra of the ceramic substrates. It has been observed that XRD peaks related to some directions are much stronger than the respective peaks observed for GaN powder. It is especially visible for the MOVPE GaN film deposited on the substrate obtained from smaller grains, where two peaks at 34.63° and 36.99° indexed as (0 0 2) and (1 0 1), respectively, are dominating. This indicates that the GaN film grows better in selected directions in this case. The other phenomenon is a narrowing of the peaks. This behavior is related to an increase in the GaN grain size. We suppose that during MOVPE deposition nanosize islands appear, but with the increase in the deposition time the size of the islands increases and they can combine to form bigger islands. Therefore, the broadening of XRD peaks decreases. For example, we have determined that the average size of GaN grains for an MOVPE film is 200 nm.

Fig. 2 shows PL spectra measured at room temperature for (i) GaN powder, (ii) GaN ceramic, (iii) MOVPE GaN film, for different sizes of the initial GaN grains. PL spectrum of GaN powder obtained at 850 °C as well as of the ceramic obtained from this powder, exhibits a broad yellow emission typical of poor-quality GaN layers. In addition, no band gap-related emission is observed. This phenomenon is associated with the very small size of GaN grains. The surface of the GaN grain is optically active and is probably one of the origins of the yellow emission. However, in the case of grains obtained at 1050 °C, the band gap-related emission is clearly observed beside the yellow PL band. Since the band gap emission is a process related to the crystal volume, a decrease in the crystal size changes the surface-to-volume ratio and hence different optical properties can be observed in different proportions. This was already discussed in detail in our previous papers [2,10]. Moreover, as it can be seen in Fig. 2(b), compressing GaN grains into ceramic changes their optical properties significantly and only the yellow emission is observed.

PL spectra for the MOVPE GaN films are different from the PL spectrum of a GaN powder and depends on the initial GaN grain sizes. In both cases a strong emission band at ~362 nm wavelength, which corresponds to the band gap of a bulk GaN, has been observed. However, the broadening of this emission in both cases is different and equal to ~30 and 15 nm for initial grains obtained at 850 and 1050 °C, respectively. Additionally, the sample obtained from bigger grains exhibits additional weak emission bands related to recombination via defect states, while in the case of the sample obtained from smaller grains this kind of emission does not appear at all.

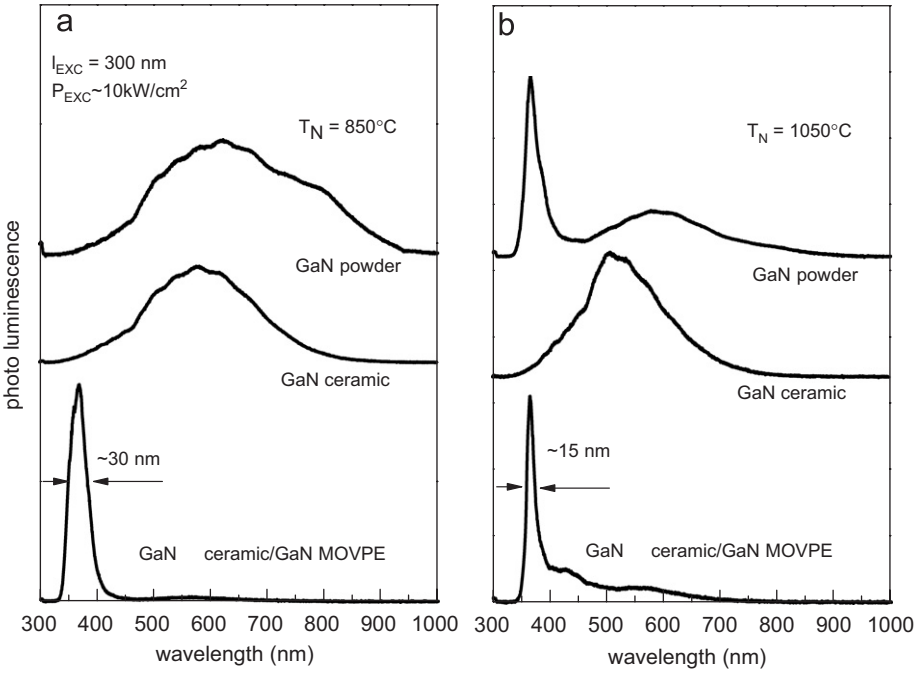

Fig. 2. PL results obtained for (a) GaN powder obtained at 850 °C, GaN ceramic, GaN film grown by MOVPE on GaN ceramic and (b) GaN powder obtained at 1050 °C, GaN ceramic, GaN film grown by MOVPE on GaN ceramic.

4. Conclusion

Summarizing the above findings, we concluded that the optical properties of MOVPE GaN films are quite satisfactory for some applications, like e.g. luminophors. The epitaxial growth of GaN films on a GaN-substrate wafer fabricated from GaN powder seems to be a very promising approach to obtain cheap GaN films with strong UV emission. It is worth noticing that the process of the film fabrication can be optimized in various ways. We can modify the powder, as well as the parameters of epitaxial growth.

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